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# TECHNICAL NOTE

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LUBRICATION OF CORROSION-RESISTANT ALLOYS BY MIXTURES OF  
HALOGEN-CONTAINING GASES AT TEMPERATURES UP TO 1200° F

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
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LUBRICATION OF CORROSION-RESISTANT ALLOYS BY MIXTURES OF  
HALOGEN-CONTAINING GASES AT TEMPERATURES UP TO 1200° F

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SUMMARY

Friction and wear experiments were conducted to explore the effects of high temperature, varied bromine content, and postulated reaction mechanisms on boundary lubrication with reactive gases. Dibromodifluoromethane ( $\text{CF}_2\text{Br}_2$ ), monobromotrifluoromethane ( $\text{CF}_3\text{Br}$ ), monobromodifluoromethane ( $\text{CHF}_2\text{Br}$ ), and sulfur hexafluoride ( $\text{SF}_6$ ) gases were used to lubricate various nickel and cobalt alloys at temperatures up to 1200° F. A 3/16-inch-radius hemispherical rider under a load of 1200 grams contacted the flat surface of a rotating disk; the usual surface speed was 120 feet per minute. In some cases the surface speed was varied.

A 1:1 gas blend of  $\text{CF}_2\text{Br}_2$  and  $\text{CF}_3\text{Br}$  was found to be an effective lubricant to 1200° F for two metal combinations, Stellite 98M2 on Hastelloy C and Inconel X on Rexalloy 33. The gases  $\text{CHF}_2\text{Br}$  and  $\text{CHF}_2\text{Br}$  plus 1 percent  $\text{SF}_6$  used to lubricate 98M2 Stellite sliding on Hastelloy C were not as effective (as lubricants) as the gas blend (1:1)  $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$ . Postulated reaction mechanisms can be used to select metal-gas combinations suitable for high-temperature lubrication systems.

INTRODUCTION

Extreme high-temperature lubrication is required for advanced types of aerodynamic and space vehicles. For example, in missile components such as turbodrives environmental temperatures from 1000° to 1800° F create an important problem area for lubrication (ref. 1). Temperatures of this magnitude are beyond the useful limit of conventional organic liquids and greases and, therefore, unconventional methods of lubrication must be sought. One method is the use of halogen-substituted methane and similar gases. A number of these gaseous compounds (e.g.,  $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{Br}_2$ ) possess extremely good thermal stability and are capable of providing effective lubrication as discussed in references 2 and 3.

The mechanism for gas lubrication is similar to that encountered in "extreme pressure" lubrication of gears where reactive compounds are used as additives to oils. The gases employed as lubricants are stable in contact with metal surfaces at ambient temperatures of 1000° F. Where metals are in sliding contact, however, extremely high flash temperatures are generated at contacting metal asperities (e.g., 1100° F above the ambient temperature in effective boundary lubrication, ref. 4). These temperatures are sufficient to cause localized decomposition of gas molecules adsorbed on the metal surface. The halogen atoms of the molecule are then free to react with the hot metal surface to form metal halides, which function as solid lubricants.

The nature of the metallic halides formed on the sliding surface and the rate at which they form determine the effectiveness of the lubrication system. When the reaction rate is exceedingly high, an excess of metallic halide may form and thus result in corrosion of the surface. For example, a corrosion problem was encountered in lubricating tool steel with a halogen-containing gas above 600° F, but the use of cobalt- and nickel-base alloys eliminated the corrosion problem (ref. 3).

In gas lubrication, where surface reactions are important, the gas must have the proper halogen content. It is necessary to have sufficient halogen present in the gaseous molecule to satisfy lubrication requirements and yet not an excess that would cause corrosion at high temperatures. The gas monobromotrifluoromethane ( $\text{CF}_3\text{Br}$ ) has a single bromine atom and provided effective lubrication at high temperatures (ref. 3). At room temperature, however, insufficient bromine was present to provide adequate lubrication. The gas dibromodifluoromethane ( $\text{CF}_2\text{Br}_2$ ) has two bromine atoms and provided effective lubrication at lower temperatures (below 800° F, ref. 3). At higher temperatures, however, corrosive wear of the metals was experienced with  $\text{CF}_2\text{Br}_2$ . One method for obtaining proper bromine content is to blend the two gases in optimum proportions; thus, it may be possible to obtain effective lubrication over a broad temperature range without corrosive wear.

A second method of attacking the problem is to select a gas that has a single bromine atom but does not possess as good thermal stability as  $\text{CF}_3\text{Br}$ . A gas molecule containing a hydrogen atom ( $\text{CHF}_2\text{Br}$ ) is less stable and should give better performance at the lower temperatures.

Gas lubrication depends on surface reactions, and postulation of the alloy combinations that can be effectively lubricated by a particular gas or gas combination would be helpful. To select these combinations without experimentation, it is necessary to understand the chemical reactions. Information on the composition of surface films and wear debris can facilitate prediction of metal-gas combinations suitable for an effectively lubricated system.

The object of the research reported herein was, first, to find optimum gas mixtures for effective lubrication of alloys over a broad temperature range and, second, to postulate reaction mechanisms in order that useful metal-gas combinations might be predicted. The gases used in this investigation were  $\text{CF}_3\text{Br}$ ,  $\text{CF}_2\text{Br}_2$ ,  $\text{CHF}_2\text{Br}$ , and  $\text{SF}_6$ . Nickel- and cobalt-base alloys were studied in gas atmospheres over the temperature range from  $75^\circ$  to  $1200^\circ$  F. Friction, wear, and corrosion characteristics were noted. In friction and wear experiments, a  $3/16$ -inch-radius hemisphere contacted the flat surface of a rotating  $2\frac{1}{2}$ -inch-diameter disk. The sliding velocity usually employed was 120 feet per minute.

### APPARATUS AND PROCEDURE

The apparatus used in this investigation (also used in ref. 2) is shown schematically in figure 1. The basic elements of the apparatus consist of a rotating-disk specimen ( $2\frac{1}{2}$ -in. diam.) and a hemispherically tipped rider specimen ( $3/16$ -in. rad.).

The rider specimen is stationary and in sliding contact with the rotating-disk specimen. The disk was rotated by means of an electric motor through a variable-speed transmission. Loads were applied to the rider specimen by means of a dead-weight system. The frictional force was measured directly by means of four strain gages mounted on a copper-beryllium dynamometer ring. The frictional force was continuously recorded on a strip-chart potentiometer. After the experiment, the wear volume was calculated from the measured diameter of the wear area on the rider specimen.

The compositions of the alloys used in the investigation are presented in the following table:

Material	Typical composition, percent by weight									Average hardness, Rockwell C-
	Fe	C	Si	Ni	Cr	Co	W	Mo	Other	
Hastelloy C	6.0	----	----	52.0	17.0	----	5.0	19.0	Mn, Si	33
Inconel X	5 to 9	0.08	0.50	70.0	15.0	----	----	----	Mn, S, Al, Cb	29
Stellite 98M2	3.0	2.0	1.0	3.5	30.5	40.0	18.5	----	B, V	52-57
Rexalloy 33	3.0	2.25	1.0	.25	32.5	44.0	17.0	----	-----	52-55

The gaseous lubricants ( $\text{CF}_3\text{Br}$ ,  $\text{CF}_2\text{Br}_2$ , and  $\text{CHF}_2\text{Br}$ ) were introduced into a 2-liter Inconel pot that (with its cover) enclosed the disk and rider specimen. The Inconel pot was heated by means of strip heaters mounted on the outer walls and concentric-ring heaters in the base of the pot. The strip and ring heaters were controlled by individual Variac units. The temperature was measured by an Inconel-sheathed Chromel-Alumel thermocouple located along the side of the disk specimen, and the temperatures were read from an indicating potentiometer. The temperatures were varied from  $75^\circ$  to  $1200^\circ$  F. The Inconel test chamber was purged for a 15-minute period prior to actual starting of the run. The specimens were brought to temperature in air before the period of purge was initiated. The gas-flow rates (1 liter/min) and mixtures used in the purge were the same as those employed in the run. At the completion of the purge, the run-in procedure was initiated. Measurements discussed in reference 2 show that less than 0.5 percent oxygen was present in the test chamber after purge and during operation with the gas  $\text{CF}_2\text{Cl}_2$ .

A run-in procedure was found necessary as a result of some previous work with  $\text{CF}_2\text{Cl}_2$  which showed that, if the run was started with high load and speed, surface failure of the specimens was apt to occur. The high initial friction and wear can be attributed to the lack of sufficient time for the formation of a reaction film. As a result it was found that, by reducing the speed and employing incremental loading, a reaction film could form which markedly reduced the initial high friction and wear.

## RESULTS AND DISCUSSION

### Lubricating Gases

Metal combinations in air. - In preliminary studies on friction and wear, experiments were conducted with two metal combinations in air at temperatures up to  $1200^\circ$  F. The data in air provided a basis of comparison for evaluating data obtained in the various reactive-gas environments. The first metal combination was 98M2 Stellite sliding on Hastelloy C in air to  $1200^\circ$  F; the friction and wear data obtained are presented in figure 2. The second metal combination was Inconel X sliding on Rexalloy 33 in air to temperatures of  $1200^\circ$  F, and the friction and wear data are shown in figure 3.

Mixtures of brominated methanes. - Data obtained in reference 3 with  $\text{CF}_3\text{Br}$  plus 1 percent  $\text{SF}_6$  and with  $\text{CF}_2\text{Br}_2$  lubricating 98M2 Stellite sliding against Hastelloy C at temperatures from  $75^\circ$  to  $1200^\circ$  F are presented in figure 4 for the purpose of comparison. The trend in the wear curve with  $\text{CF}_3\text{Br}$  acting as the lubricant indicates an increasing effectiveness with increase in temperature. The wear obtained with  $\text{CF}_2\text{Br}_2$  functioning as the lubricant was low to a temperature about  $800^\circ$  F, above which the wear began to increase, reflecting the influence of corrosion.

The reversal in wear trends suggested that a mixture of the two gases might provide intermediate wear values over the entire temperature range. The two gases  $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{Br}_2$  were mixed in varying percentages and used to lubricate 98M2 Stellite rider sliding on Hastelloy C disk at room temperature and  $1200^\circ\text{F}$ . The results of these experiments are presented in figure 5. The wear and friction data indicate that, at both temperatures, an equal (1:1) mixture of the two gases merits consideration for additional study.

The 1:1 gas mixture  $\text{CF}_3\text{Br}:\text{CF}_2\text{Br}_2$  was used to lubricate the 98M2 Stellite rider sliding on the Hastelloy C disk over the temperature range from  $75^\circ$  to  $1200^\circ\text{F}$ . The friction and wear data for the metals sliding in this atmosphere are given in figure 6. The friction data represent an approximate mean of the values obtained with the individual gases. However, the wear with the mixture was lower at all temperatures than that obtained with either of the gases alone. Thus, the gas blend seems to produce a synergistic effect. The relative independence of wear with respect to varied temperatures (fig. 6) may be explained in terms of the bromine available for surface reaction. At the lower ambient temperatures, where a single bromine atom was inadequate, there was a 25-percent increase in bromine available from the blend for surface reaction. At higher temperatures, however, the bromine content of the blend was 25 percent less than that available with the dibrominated gas, and therefore a reduction in corrosive wear was observed. Thus, an effective balance between adhesive and corrosive wear was achieved.

The rider wear (over entire temperature range) with the gas mixture was approximately 1 percent of the wear obtained in air (fig. 6). A considerable reduction in friction was also observed.

The results obtained with mixtures of gases containing bromine warranted an investigation of the apparent optimum mixture at sliding velocities other than 120 feet per minute. The results of experiments to show the influence of sliding velocity are presented in figure 7. The five sliding velocities investigated (55 to 5200 ft/min) seem to show little influence on friction coefficient over the temperature range ( $75^\circ$  to  $1200^\circ\text{F}$ ) studied.

An incompletely halogenated methane. - The effectiveness of the bromine-containing gas mixture as a lubricant can be attributed to the amount of bromine made available for surface reaction, and this quantity is dependent on the thermal stability of the gaseous molecule. A gas that contains a single bromine atom but does not possess as good thermal stability as  $\text{CF}_3\text{Br}$  might be as effective a lubricant as the gas blend. A single bromine-containing methane derivative that is not quite as stable as  $\text{CF}_3\text{Br}$  is  $\text{CHF}_2\text{Br}$ . With the gas  $\text{CHF}_2\text{Br}$  and the same metal combination (98M2 Stellite rider sliding on Hastelloy C disk), friction and wear experiments were conducted at temperatures from  $75^\circ$  to  $1200^\circ\text{F}$ . The

results of these experiments are presented in figure 8. The presence of hydrogen in the molecule made it difficult to obtain reproducible results. This can be attributed to the formation of hydrobromic acid (HBr) as one of the gaseous decomposition products, which is corrosive to the metal surfaces.

For purposes of comparison, friction and wear experiments were made with  $\text{CHF}_2\text{Br}$  plus 1 percent  $\text{SF}_6$  with the same metal combinations. Tests were run at  $75^\circ$ ,  $600^\circ$ , and  $1000^\circ$  F. The results obtained are presented in figure 9 and are compared with data for  $\text{CF}_3\text{Br}$  plus 1 percent  $\text{SF}_6$  from reference 3. The results indicate that the hydrogen-containing gas  $\text{CHF}_2\text{Br}$  plus 1 percent  $\text{SF}_6$  is effective in reducing friction and wear at  $75^\circ$  F. At the higher temperature, however, the wear increases rather markedly. The friction and wear trends obtained with  $\text{CF}_3\text{Br}$  plus 1 percent  $\text{SF}_6$  decrease as the temperature is increased.

#### Film-Formation Mechanisms

Chemical mechanism. - The selection of optimum gas-slider material combinations is critical in reactive gas lubrication. Previous experience in fundamental studies of solids (ref. 5) and reaction gases (refs. 2 and 3) as lubricants has suggested desirable end products in surface reactions with gas lubricants. Metals normally have passive oxide layers. Therefore, the reaction mechanisms of importance are concerned with the oxide films as well as the nascent metals. The relative chemical activity of the various alloy constituents is also a basic consideration. The local energy level at the slider interface (produced by pressure equal to the yield stress in compression for the alloys and by temperatures that are apt to be more than  $1000^\circ$  F above the ambient) causes a highly active chemical state that results in reactions going to completion. The chemistry at the slider interface is exceedingly complex because of the magnitude of variables present. A relatively simple consideration of the possible thermochemical processes, however, can do much to clarify the surface reactions. Such considerations are reported in the appendix. Selection of promising gas-slider material combinations may be based on these postulated reactions.

Physical mechanism. - A physical consideration of the sliding process between two metals of different hardness suggests that the softer metal may have more nascent metal exposed. Plastic deformation of the softer metal causes rupture of the passive surface layer (oxide) to expose the more active (nascent) substrate metal. Thus, when the metals are exposed to a reactive gas lubricant, the greater availability of metal cations for chemical reaction would be from the softer metal. In addition, the sustained higher temperature level of a surface in continuous sliding contact (rider specimen) would make it more active chemically than a

surface undergoing thermal cycling with the lower mean temperature that results from intermittent sliding contact (disk specimen). These concepts may provide additional physical means for control of the location and amount of surface reactions.

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The use of the forementioned chemical and physical concepts can be demonstrated. For example, nickel bromide is an effective solid lubricant and, therefore, would be a desirable surface film in reactive gas lubrication. In accordance with the reactions suggested in the appendix and the physical concepts discussed herein, an Inconel X (nickel-chromium alloy) rider specimen in sliding contact with a harder metal (Rexalloy 33) disk specimen and exposed to a reactive gas containing bromine (1:1 mixture of  $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{Br}_2$ ) might be expected to develop an effective reaction-film lubricant. Experiments run at temperatures from  $75^\circ$  to  $1200^\circ$  F with those materials gave the friction and wear data presented in figure 10. For the purpose of comparison, the data obtained with the reactive gas are presented in figure 10 together with data obtained with air (from fig. 3). Photomicrographs of a disk surface after a lubrication experiment with the bromine-containing gas are shown in figure 11. The bromide reaction film was removed with ethyl alcohol, and it was apparent that the lubrication had prevented any significant wear of the disk. Although effective lubrication was obtained with the reactive gas lubricant (fig. 10), wear of the rider specimen increased at temperatures above  $800^\circ$  F because of excessive surface reaction (i.e., corrosive wear).

Applying the physical concepts previously discussed would suggest that, if the specimens were reversed so that the rider were the harder alloy and the disk were the softer (reacting) alloy (where intermittent contact would reduce the reaction rate), corrosive wear could be decreased. In effect, the sort of system thus suggested is exemplified by the data obtained with the hard 98M2 Stellite (cobalt-base alloy) rider sliding on the softer Hastelloy C (nickel-chromium alloy) in the bromine-containing gas mixture, shown in figure 6. In figure 6 there is no increase in wear at the higher temperatures.

From the mechanism involved in gas lubrication and a knowledge of the thermochemical data for metal halides, it is possible to predict and eliminate systems that will not lubricate. An example of such a system is one in which the metal halide formed is volatile and leaves the surface film (e.g.,  $\text{MoBr}_4$  or  $\text{WBr}_4$ ). In experiments conducted with tungsten carbide, friction and wear data obtained indicated that a bromine-containing gas would not lubricate tungsten carbide. The tungsten bromide formed by the gas volatilized and left a carbon film on the surface of the material.



## SUMMARY OF RESULTS

From the experimental results obtained in the research reported herein, the following summary remarks can be made:

1. An optimum halogen concentration in reactive gases for lubrication can be obtained by selective blending of various gases. The  $\text{CF}_2\text{Br}_2$ : $\text{CF}_3\text{Br}$ (1:1) mixture is an excellent gas blend for 98M2 Stellite sliding on Hastelloy C and for Inconel X sliding on Rexalloy 33 at temperatures from 75° to 1200° F.

2. The use of physical properties of alloys and reaction mechanisms in gas lubrication is an aid in the selection of metal-gas combinations for lubrication systems. Alloy-gas combinations that will form reaction films having desirable lubricating properties can be selected.

3. A gas with a less stable molecular configuration such as  $\text{CHF}_2\text{Br}$  was not quite as effective a lubricant as the fully halogenated gases  $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{Br}_2$ . The presence of hydrogen in the molecule results in the formation of hydrogen bromide (HBr) when the gaseous molecule decomposes. An atmosphere including hydrobromic acid resulted in severe corrosion to the metals being lubricated.

Lewis Research Center

National Aeronautics and Space Administration  
Cleveland, Ohio, September 2, 1959

## APPENDIX - REACTIONS IN FILM FORMATION

Very little thermochemical data are available in the literature for metal oxides and halides. The data are even more difficult to obtain for materials at elevated temperatures. In postulating chemical reactions occurring in gas lubrication, a knowledge of thermochemical values for various metal oxides and bromides becomes imperative. The standard free energy of formation for various metal oxides up to a temperature of 2000° K is presented in figure 12 and is taken from reference 6. In order to obtain the standard free energy of formation ( $\Delta F^\circ$ ) for metal bromides, calculations had to be made from data obtained in reference 7. The values of  $\Delta F^\circ$  at temperatures to 2000° K with corresponding melting and boiling points are presented in figure 13. The  $\Delta F^\circ$  values are in kcal per gram-atomic weight of cation or metal ion; they were plotted in this manner to facilitate a direct comparison of the relative stabilities of the various compounds. Since the lower the curve, the more stable the compound formed, a direct visual comparison of the relative stabilities of the metallic halides can be made from the graphs. The simple thermodynamic relations used in these calculations are:

$$\Delta F_{298}^\circ = \Delta H - T \Delta S \quad (A1)$$

Since  $\Delta H^\circ$  is constant and  $\Delta S^\circ$  changes to a minor extent only with a change in temperature (provided the reactants and products undergo no phase changes), a plot of  $-\Delta F^\circ$  against  $T$  results in lines that are very nearly straight with a slope of  $+\Delta S^\circ$  (ref. 8). Therefore,

$$\Delta S = \frac{\Delta F_{T,2}^\circ - \Delta F_{T,1}^\circ}{T_2 - T_1} \quad (A2)$$

Then,  $\Delta F^\circ$  at any temperature  $T_2$  can be calculated from a knowledge of  $\Delta S$  and  $\Delta F^\circ$  at any temperature  $T_1$  as long as no change of state occurs between  $T_1$  and  $T_2$ ; that is,

$$\Delta F_{T,2}^\circ = \Delta F_{T,1}^\circ + \Delta S_0(T_2 - T_1) \quad (A3)$$

For a temperature range from melting to boiling point,

$$\Delta F_{T,2}^\circ = \Delta F_{mp}^\circ + \Delta S_1(T_2 - T_{mp}) + \Delta F_M^\circ \quad (A4)$$

For temperatures above boiling point,

$$\Delta F_{T,2}^{\circ} = \Delta F_{T,bp}^{\circ} + \Delta S_2(T_2 - T_{bp}) + \Delta F_v \quad (A5)$$

where

$\Delta F_{298}^{\circ}$  standard free energy of formation at 298° K

$\Delta F_T^{\circ}$  standard free energy of formation at some temperature other than 298° K

$\Delta F_M$  free-energy change involved in melting ( $\Delta F$  of fusion)

$\Delta F_v$  free-energy change involved in vaporization

$T_2, T_1$  temperatures, °K

$\Delta S_0$  entropy, cal/°K

$\Delta S_1$  entropy, cal/°K from melting to boiling points

$\Delta S_2$  entropy, cal/°K above boiling point

To obtain  $\Delta F$  for a given reaction from  $\Delta F^{\circ}$ , the correction term must be made for the concentration of reactants and products. For any reaction such as  $aA + bB = cC + dD$ , the value  $\Delta F$  is calculated according to the following equation:

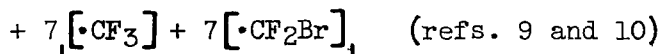
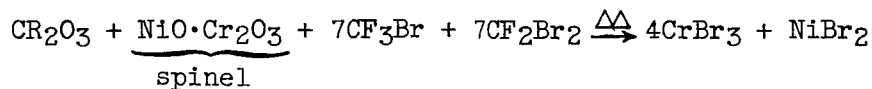
$$\Delta F = \Delta F^{\circ} + RT \ln \left[ \frac{(C)^c (D)^d}{(A)^a (B)^b} \right]. \quad \text{The standard}$$

free energies of formation serve to indicate the tendency, or lack thereof, of metal oxides and bromides to form. They also indicate the stability of the compounds and where substitution can occur. These free-energy values do not, however, indicate reaction rate, and the chemical kinetics must be known before any quantitative predictions can be made.

#### Stellite 98M2 on Hastelloy C Lubricated by $CF_2Br_2:CF_3Br$

In the Stellite 98M2 rider and Hastelloy C disk combination, the rider specimen is the harder of the two materials. The disk specimen furnishes the major portion of cations for metal halide formation. The alloy Hastelloy C is composed chiefly of Ni, Cr, W, Mo, and Fe. The principle reactions believed to occur at the sliding metal interface with the bromine-containing gas blend  $CF_2Br_2:CF_3Br$  are:

Initial surface reaction with passive oxides present on metal surface,



(1) Radical coupling - polymerization

(2) Radical decomposition

(3) Radical disproportionation

(4) Removal as radical

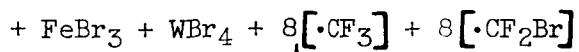
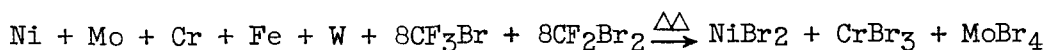
or

(5) Redox process

(A6)

Although the chrome oxide in equation (A6) is more thermodynamically stable than chrome bromide, as indicated in figure 12, it is possible as discussed by Kellogg (ref. 8) for partial substitution to occur in a dense halogen atmosphere. The concentration of reactants and products is extremely important in thermodynamic considerations, since proper adjustment of concentrations can result in a reaction that will not occur under standard thermodynamic conditions (i.e., unit activity of reactants and products). This indicates that the given reactions account in part for what occurs to the tenacious oxide present on the metal surface. Once the rider specimen has traversed the disk and the passive layer has been removed, the reactions are principally one of the alloy constituents with halogen-containing gas. The temperatures encountered at contacting metal surfaces are extremely high. Under the test condition of the friction and wear experiments, temperatures as high as 1100° F above the ambient are reported in reference 4. When the ambient temperature is 1000° F, temperatures at sliding metal interfaces may well exceed 2000° F. At this temperature the reaction rates are not critical, since all metals in the alloy should appear in the wear debris as metallic halides.

The following reactions are believed to occur with the alloy constituents and halogen-containing gas  $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$  after the passive layer has been removed:



See free-radical  
reactions (A6)

(A7)

The theoretical, as well as actual, percent of reaction products obtained in an experimental run at 1000° F is presented in the following table:

Hastelloy C		Reaction product in $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$	Theoretical composition of surface film (assume complete halogenation)	Actual analysis of reaction product, percent by weight
Constituent	Percent in alloy			
Ni	52.0	$\text{NiBr}_2$	39.50	81.0
Cr	17.0	$\text{CrBr}_3$	17.20	14.0
Fe	6.0	$\text{FeBr}_3$	6.40	4.60
W	5.0	$\text{WBr}_4$	8.75	{ Volatile halides below 600° F present only in traces
Mo	19.0	$\text{MoBr}_4$	27.30	
Traces of Mn, Si	----	-----	-----	-----

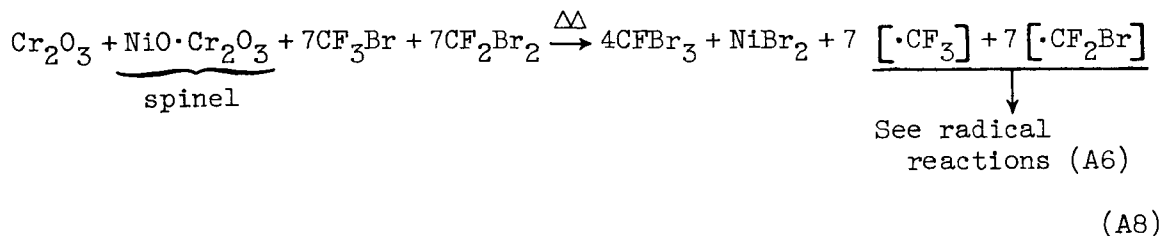
This table indicates that nickel bromide is the principal component of the wear debris. The actual percent of nickel bromide is, however, out of proportion to the theoretically calculated values. The actual composition as determined by chemical analysis could result from the volatile nature of the molybdenum and tungsten bromides. The molybdenum and tungsten bromides are volatilized from this surface film, which allows the nickel bromide concentration to increase. The nickel, iron, and chrome bromides were identified as hydrates by X-ray analysis. The reason for their existence in the hydrated form lies in the fact that the specimens were cooled in room air without moisture control and the bromide hydrated.

The other metal halides were not identified by X-ray analysis because of relatively small percentage but were detected in chemical tests.

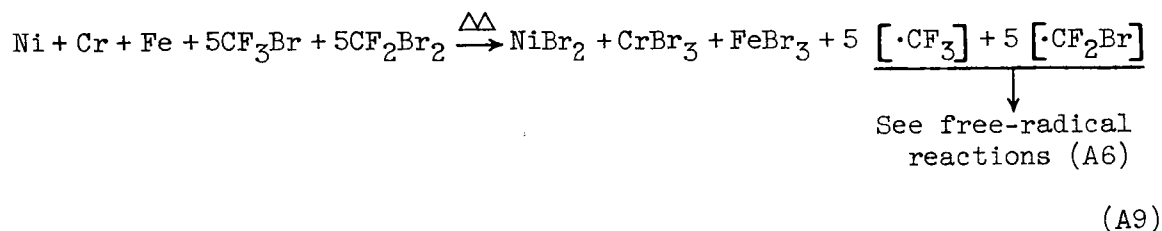
#### Inconel X on Rexalloy 33 in $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$

In the metal combination of Inconel X rider sliding against a Rexalloy 33 disk, the rider specimen is the softer of the two materials and furnishes the major portion of the cation for surface reaction (see photomicrograph, fig. 11). The elements contained in the Inconel X rider alloy are principally Ni, Cr, and Fe. When these metals react with the halogen-containing gas blend  $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$ , the following reactions are believed to occur:

Initial surface reactions with passive oxides present on metal surfaces,



Reactions with alloy constituents after passive oxide has been removed,



The theoretical as well as actual percent of reaction products obtained in an experimental run at 1000° F is presented in the following table:

Inconel X		Reaction product in $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$	Theoretical composition of surface film (assume complete halogenation)	Actual analysis of reaction product, percent by weight
Constituent	Percent in alloy			
Ni	70.0	NiBr <sub>2</sub>	64.60	66.60
Cr	15.0	CrBr <sub>3</sub>	18.40	22.0
Fe	9.0	FeBr <sub>3</sub>	11.20	9.12
Traces of C, Si, Mn, S, Al, Cb	----	-----	-----	-----

This table indicates close correlation between the actual percent of metal bromides obtained in chemical analysis and the theoretically calculated values.

The ability to determine an effective gas-lubrication system depends upon a number of factors as indicated herein. The materials to be

lubricated must possess good corrosion resistance (e.g., nickel-containing alloys) and yet must be active enough to supply metal cations for surface reaction. In the lubrication of alloys, the alloy constituents must be considered with a regard for surface reactions. The principal cation of the alloy must form a metal halide that has lubricating properties (e.g.,  $\text{NiBr}_2$ ). The thermochemical properties must also be considered to insure that at operating temperatures the metal halides formed are not all volatile (e.g., molybdenum and tungsten bromides volatile above  $660^\circ\text{F}$ ). In addition, some consideration must be given to the physical concepts, such as hardness. It is important that the softer of the two materials in sliding contact form a metal halide that has lubricating properties, since it furnishes the major portion of cations for film formation.

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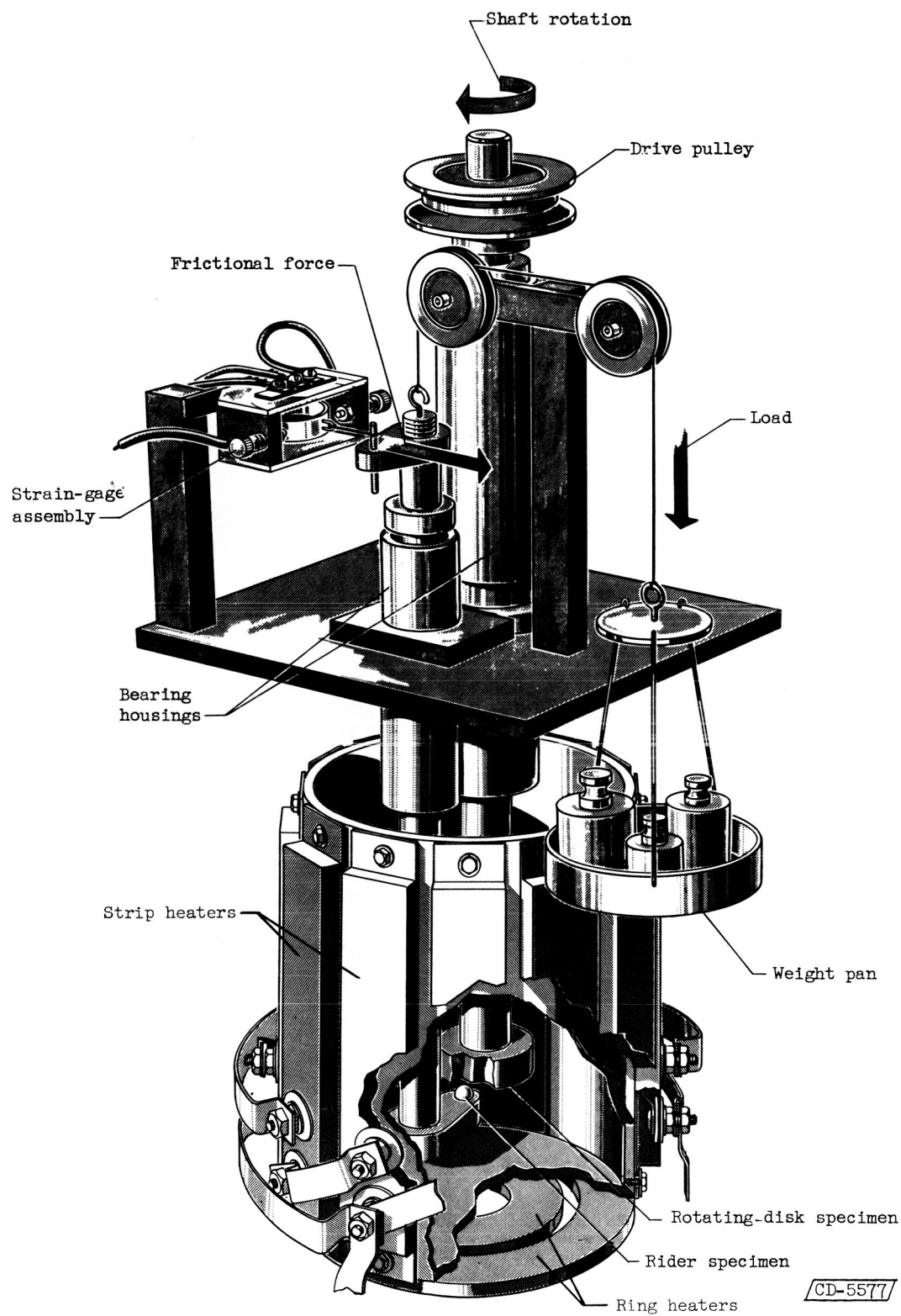


Figure 1. - Friction apparatus.



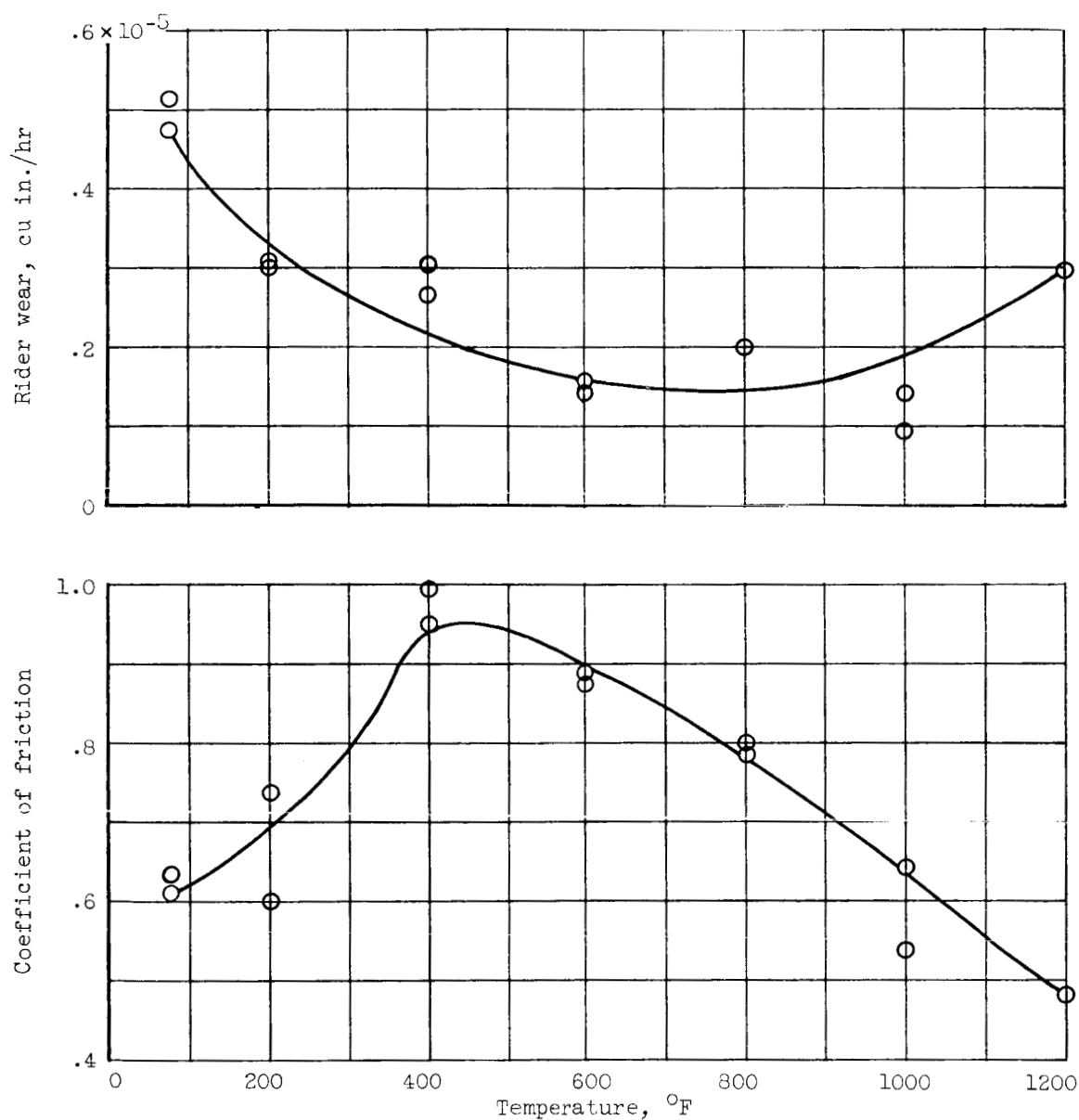


Figure 2.- Friction and wear of 98M2 Stellite rider sliding on Hastelloy C disk at various temperatures in air. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.

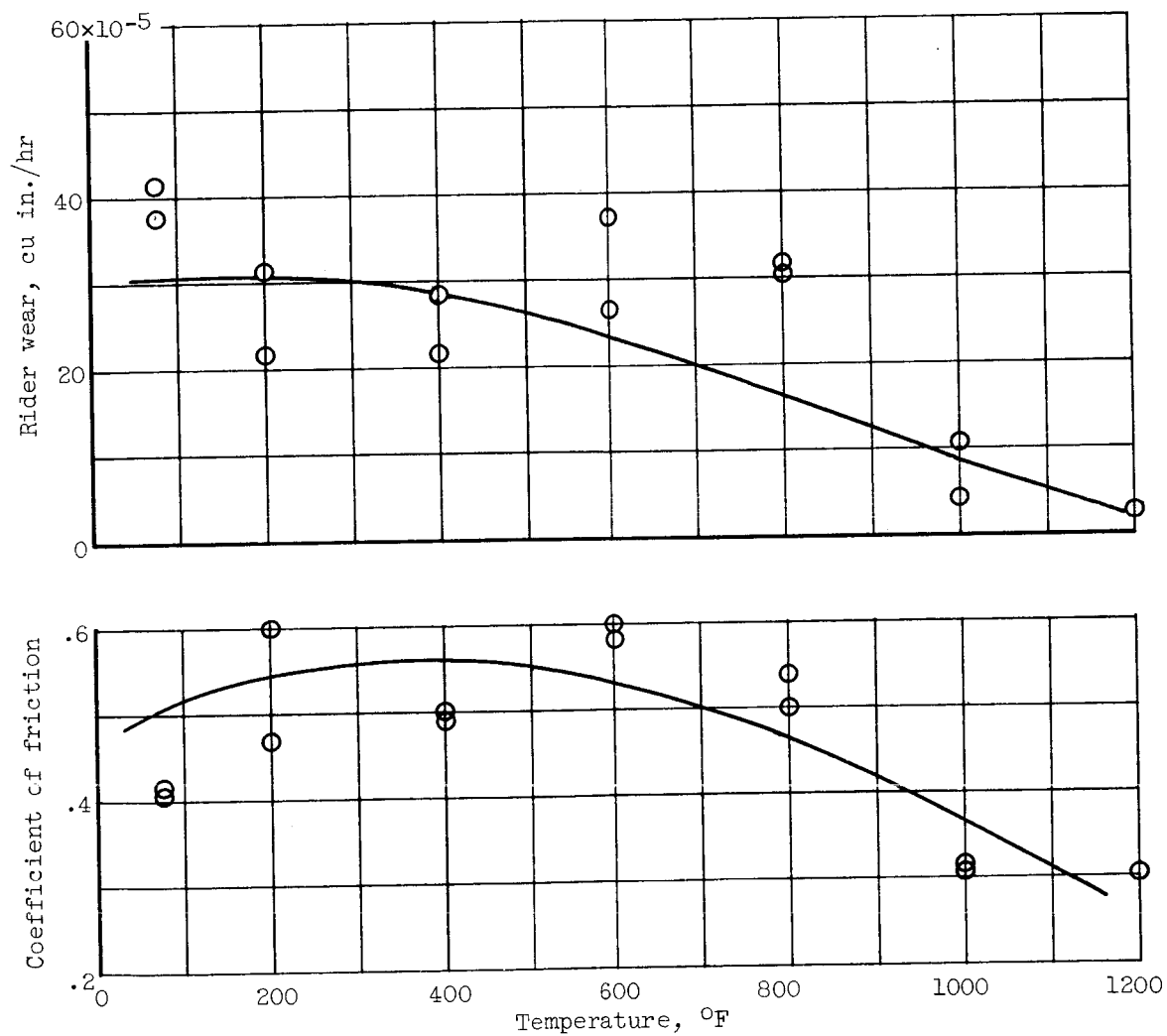


Figure 3. - Friction and wear of Inconel X rider sliding on Rexalloy 33 disk at various temperatures in air. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.

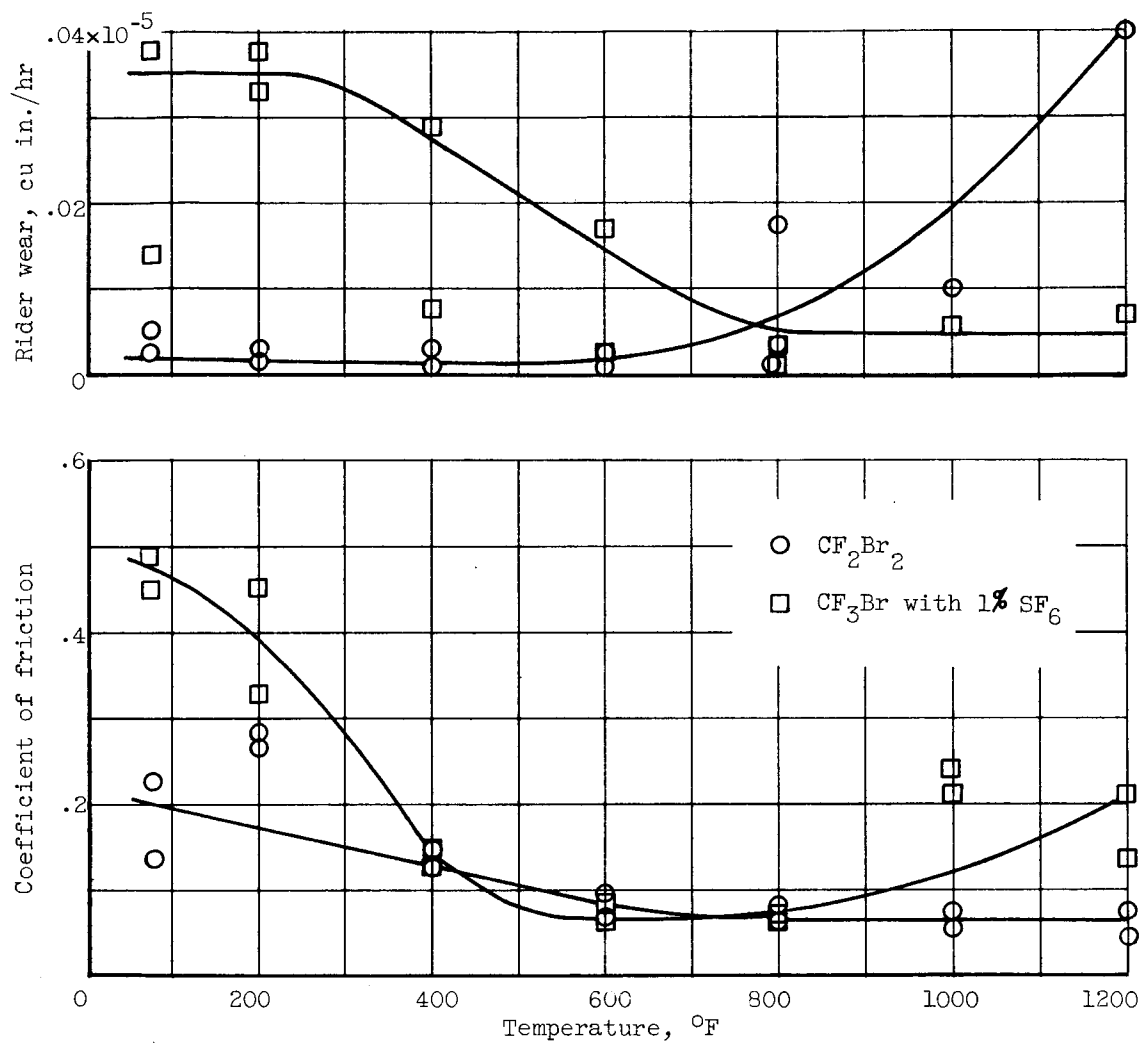


Figure 4. - Friction and wear data (ref. 3) for 98M2 Stellite rider sliding on Hastelloy C disk with  $\text{CF}_3\text{Br}$  + 1 percent  $\text{SF}_6$  and  $\text{CF}_2\text{Br}_2$  as lubricants. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.

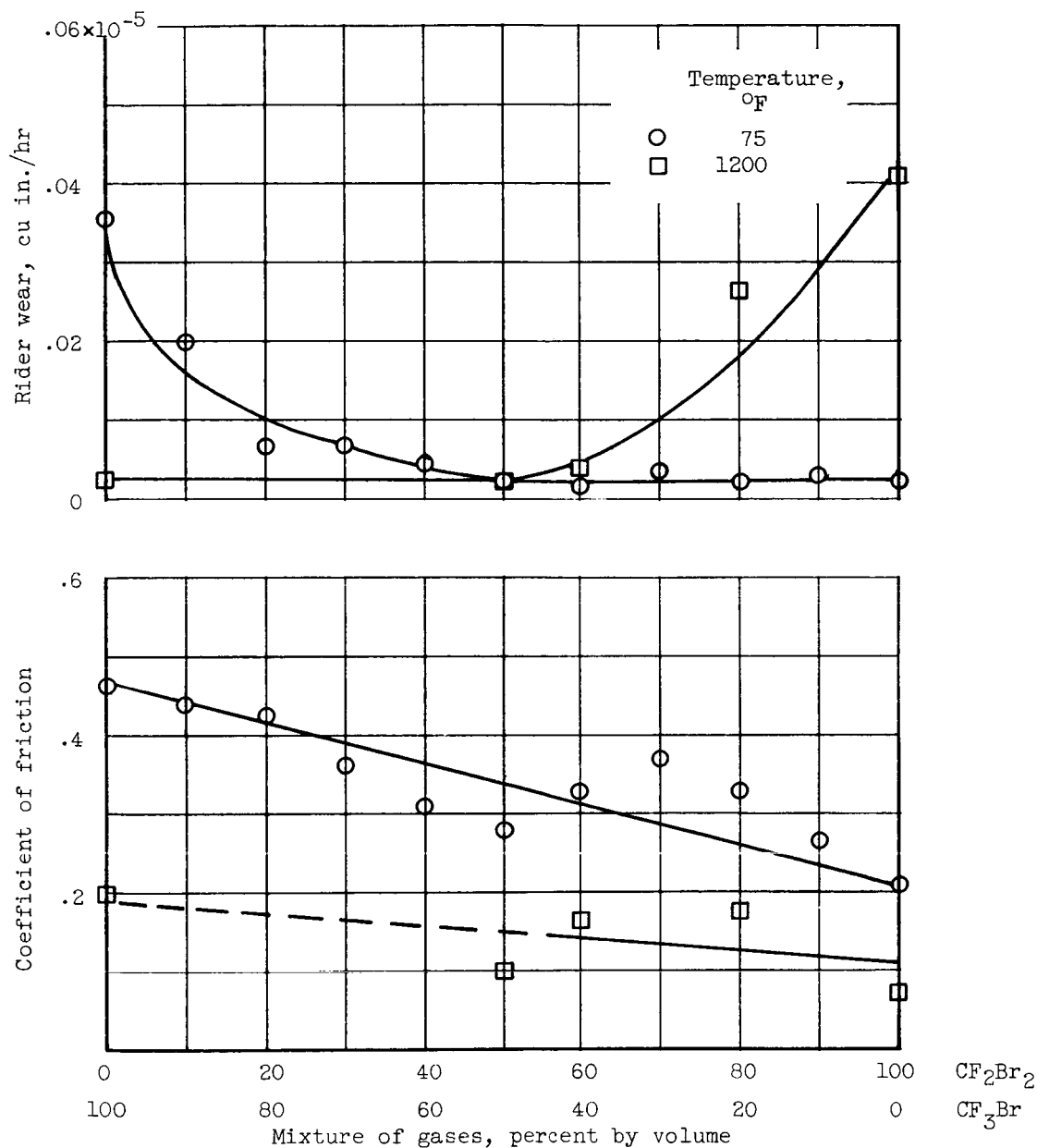


Figure 5. - Friction and wear of 98M2 Stellite rider sliding on Hastelloy C disk with various percent mixtures of the gases CF<sub>2</sub>Br<sub>2</sub> and CF<sub>3</sub>Br as lubricant. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.

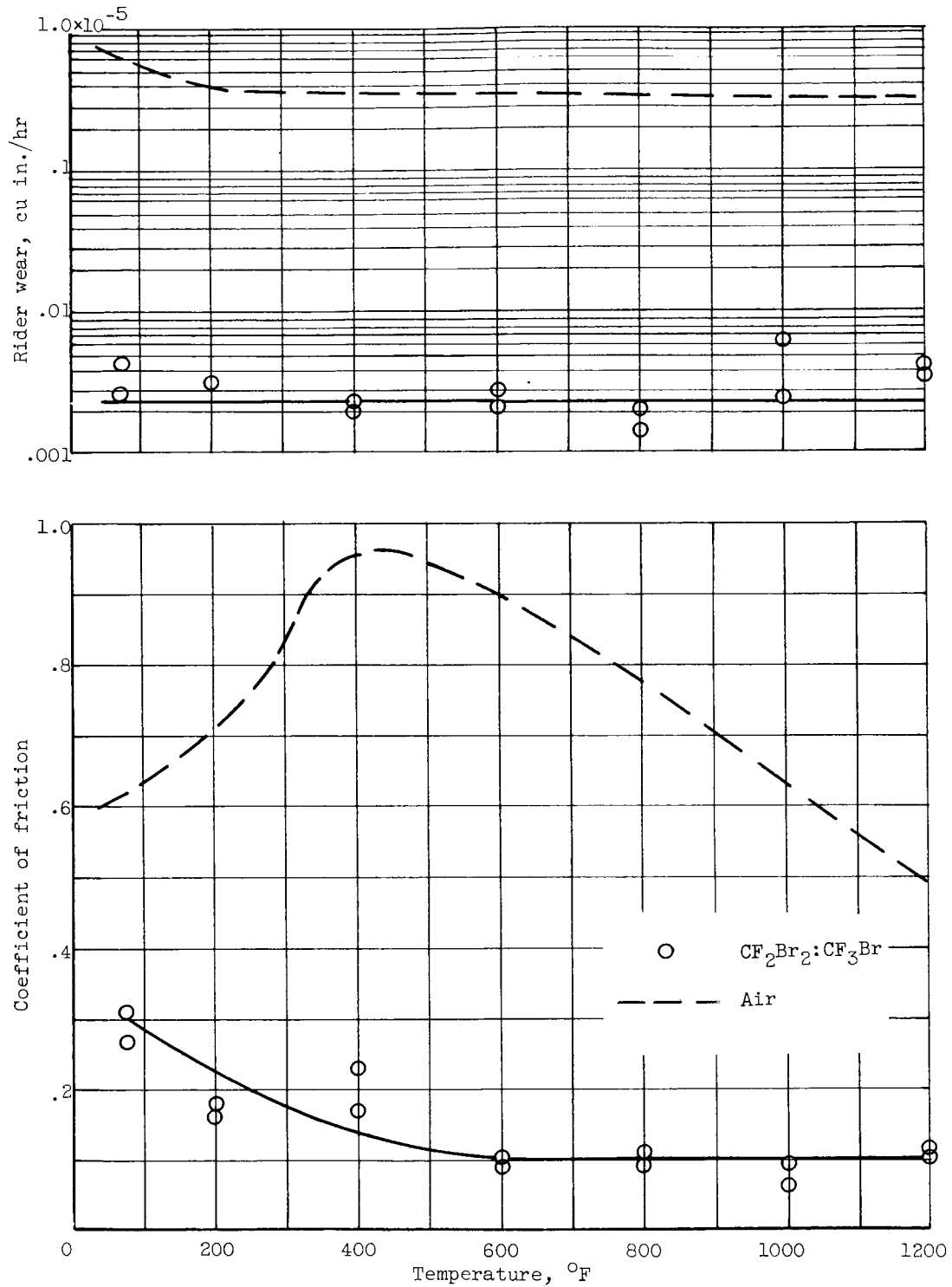


Figure 6. - Comparison of friction and wear of 98M2 Stellite rider sliding on Hastelloy C disk at various temperatures in air and with  $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$  (1:1) as lubricant. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.

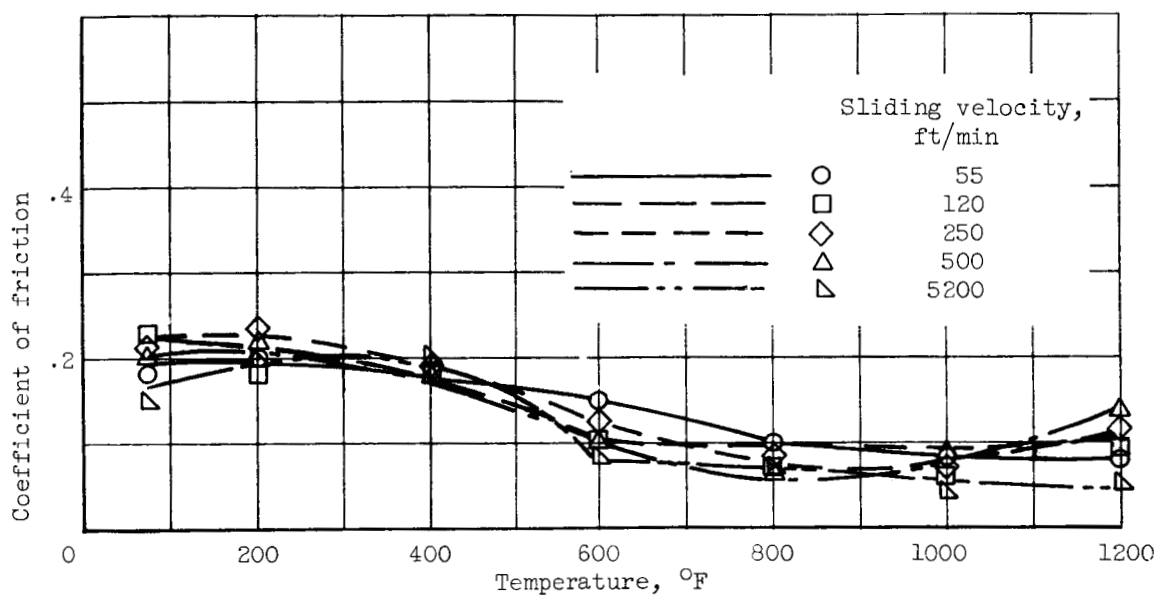


Figure 7. - Friction of 98M2 Stellite rider sliding on Hastelloy C disk at various temperatures and sliding velocities with 1:1 gas mixture of  $\text{CF}_2\text{Br}_2$  and  $\text{CF}_3\text{Br}$  as lubricant. Load, 1200 grams; duration, 1 hour.

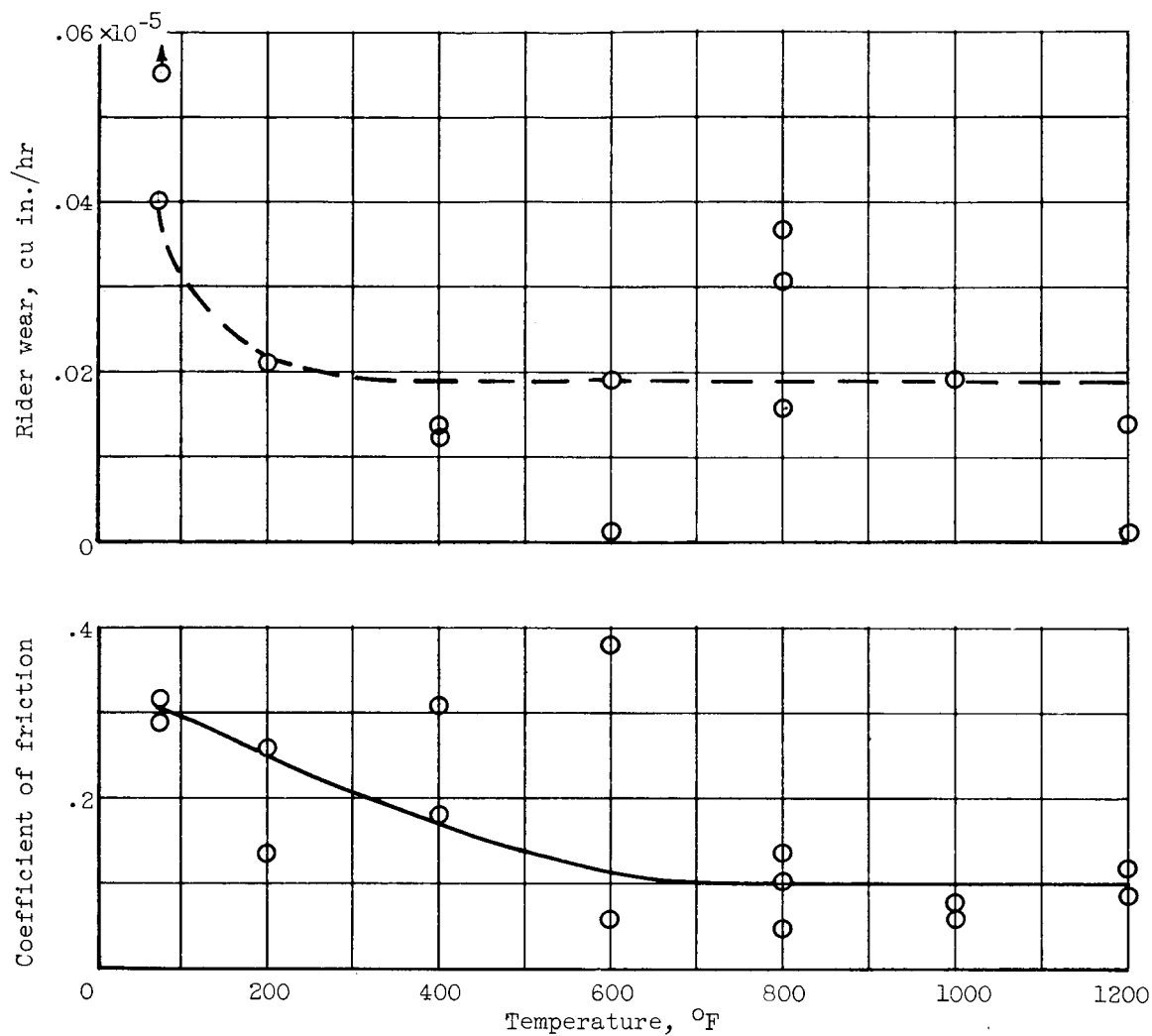


Figure 8. - Friction and wear of 98M2 Stellite rider sliding on Hastelloy C disk at various temperatures with  $\text{CHF}_2\text{Br}$  as lubricant. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.

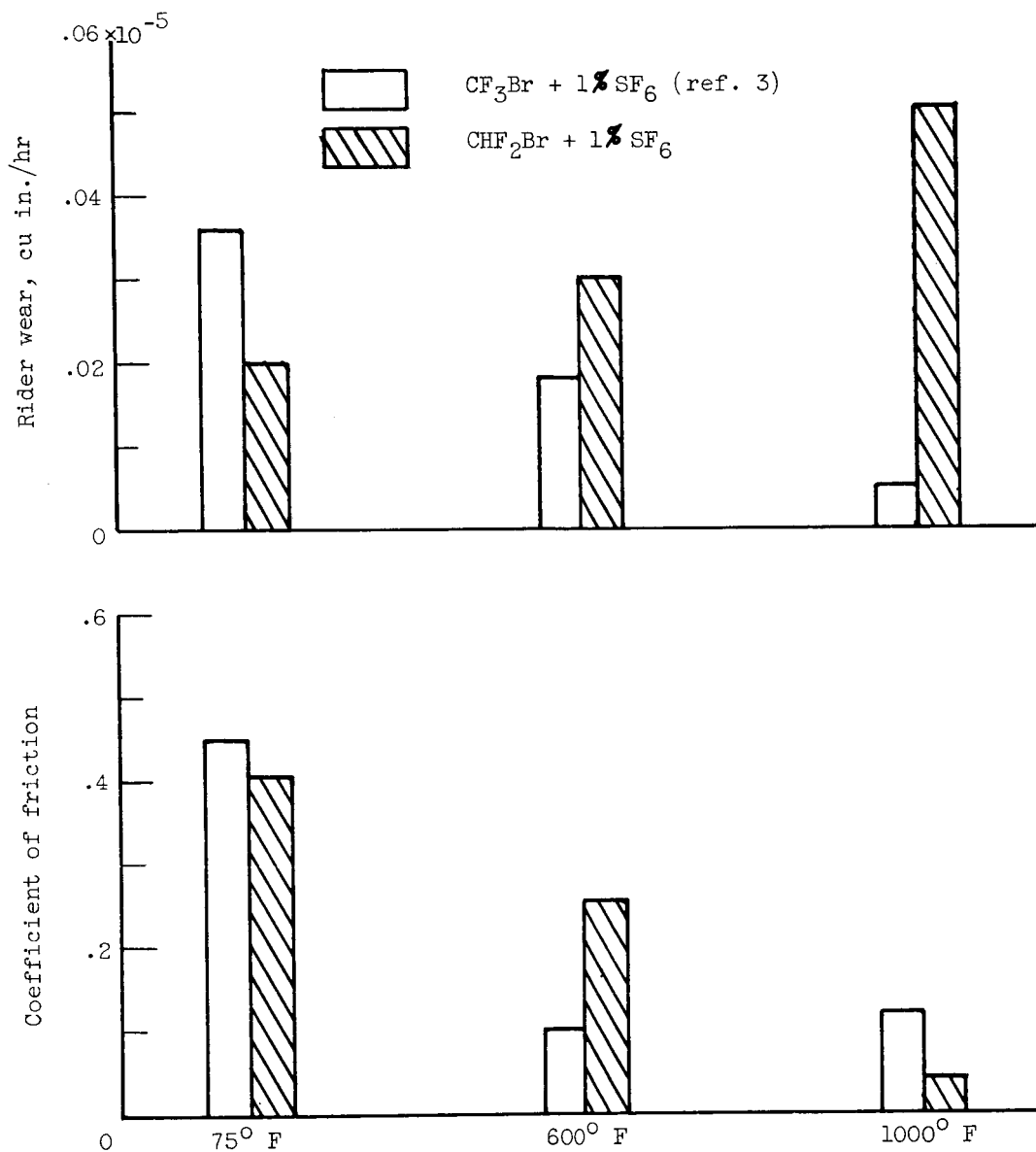


Figure 9. - Friction and wear of 98M2 Stellite rider sliding on Hastelloy C disk at various temperatures with  $\text{CF}_3\text{Br} + 1$  percent  $\text{SF}_6$  and  $\text{CHF}_2\text{Br} + 1$  percent  $\text{SF}_6$  as lubricants. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.



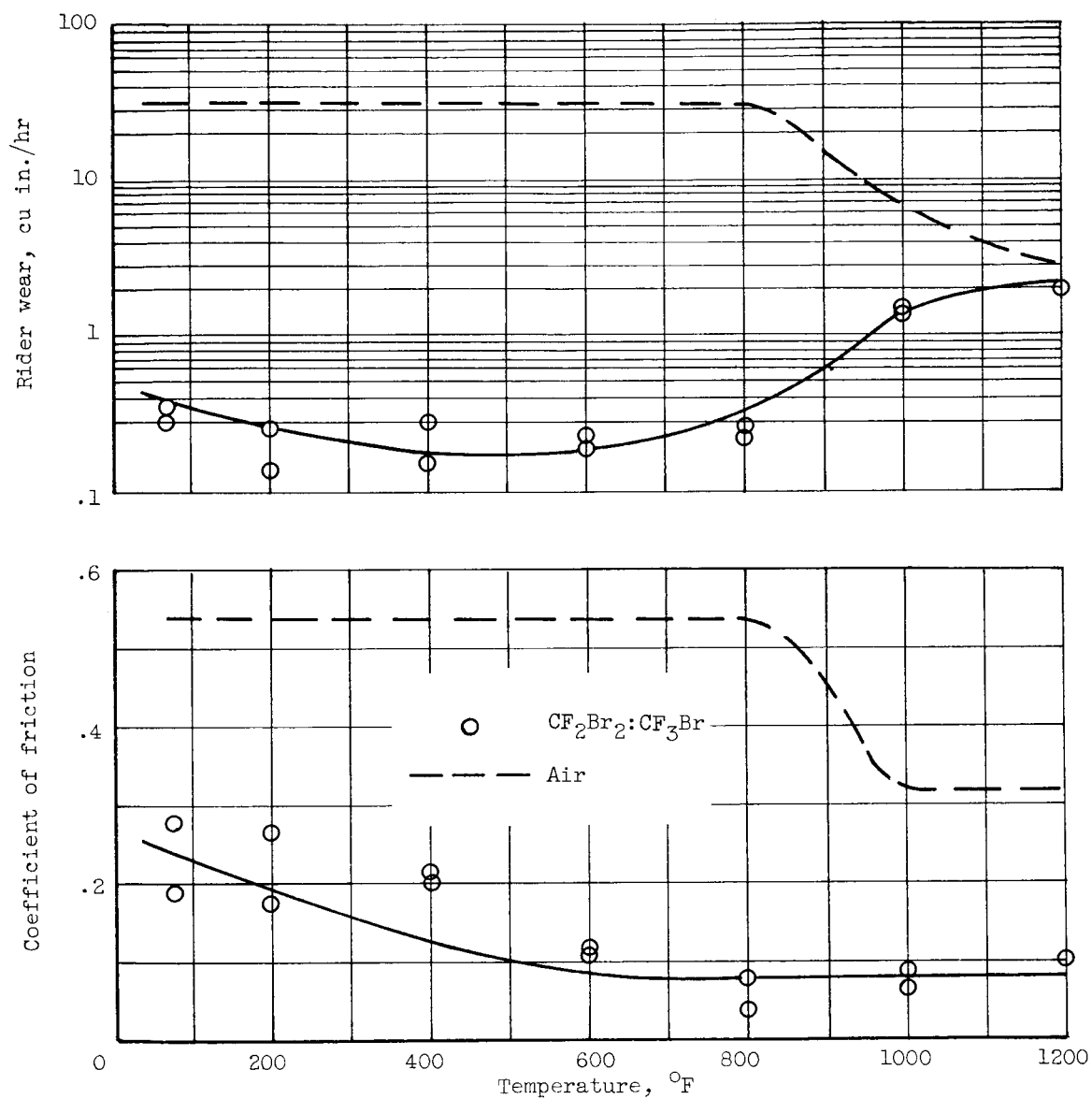
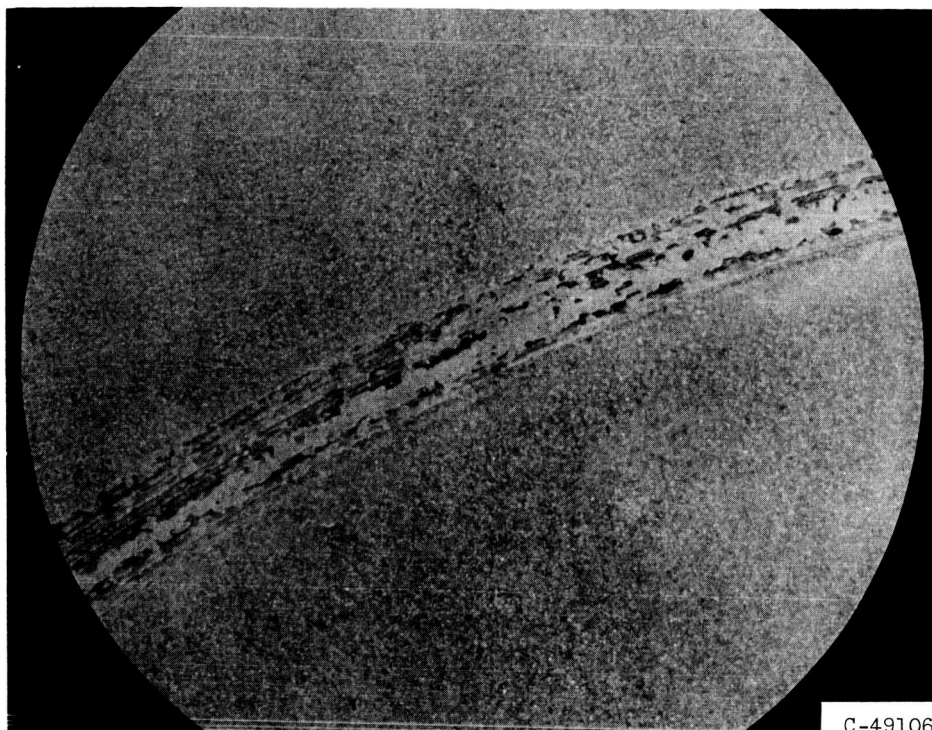
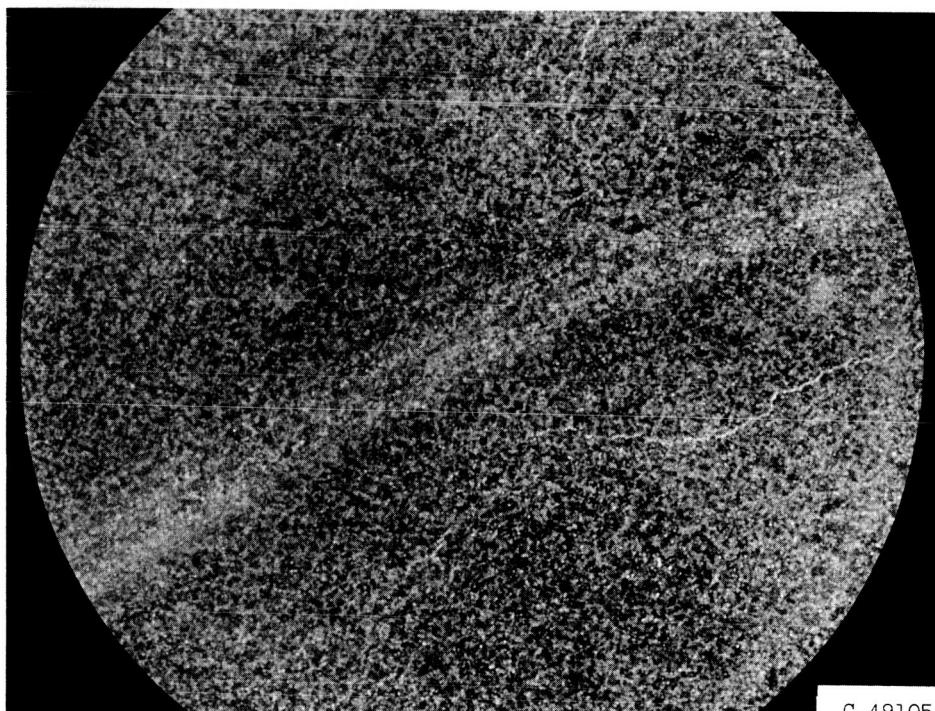


Figure 10. - Comparison of friction and wear of Inconel X rider sliding on Rexalloy 33 disk at various temperatures in air and with  $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$  (1:1) as lubricant. Sliding velocity, 120 feet per minute; load, 1200 grams; duration, 1 hour.



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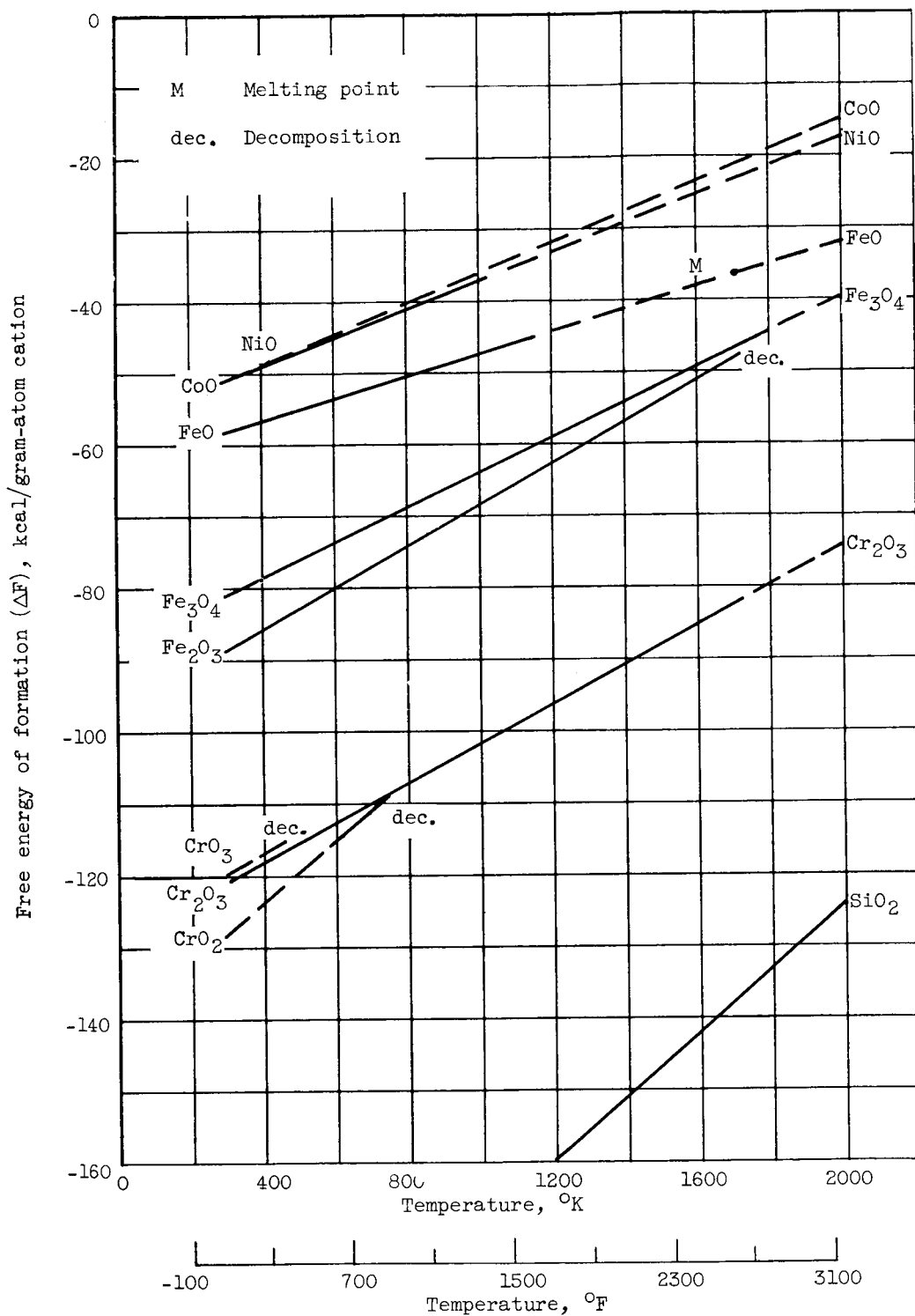
(a) Bromide film on wear track.



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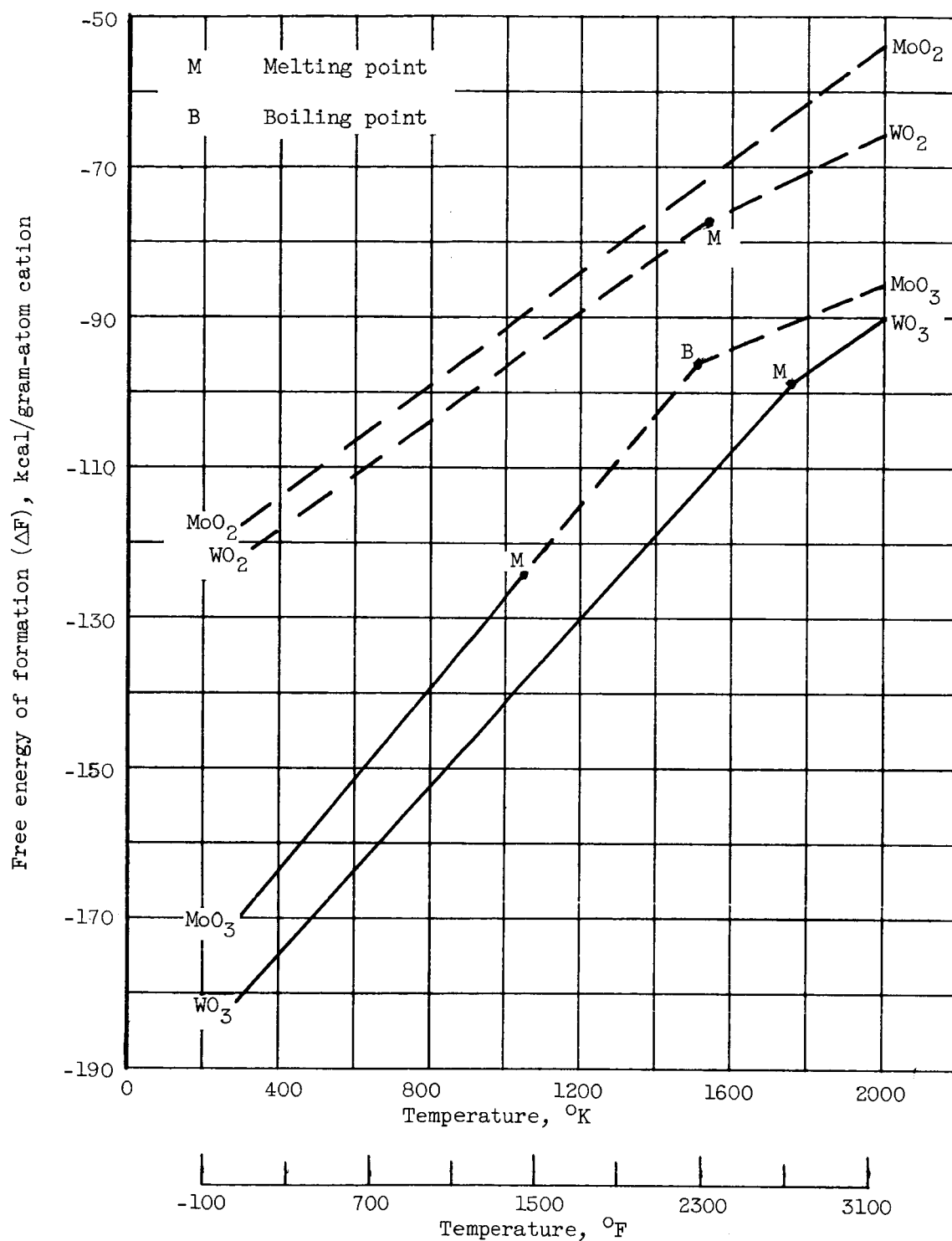
(b) Film removed with ethyl alcohol.

Figure 11. - Photomicrographs of Rexalloy 33 disk surface. Rider, Inconel X; gas (1:1),  $\text{CF}_2\text{Br}_2:\text{CF}_3\text{Br}$  mixture; load, 1200 grams; sliding velocity, 120 feet per minute; duration, 1 hour; temperature,  $800^\circ\text{F}$ ; X15.



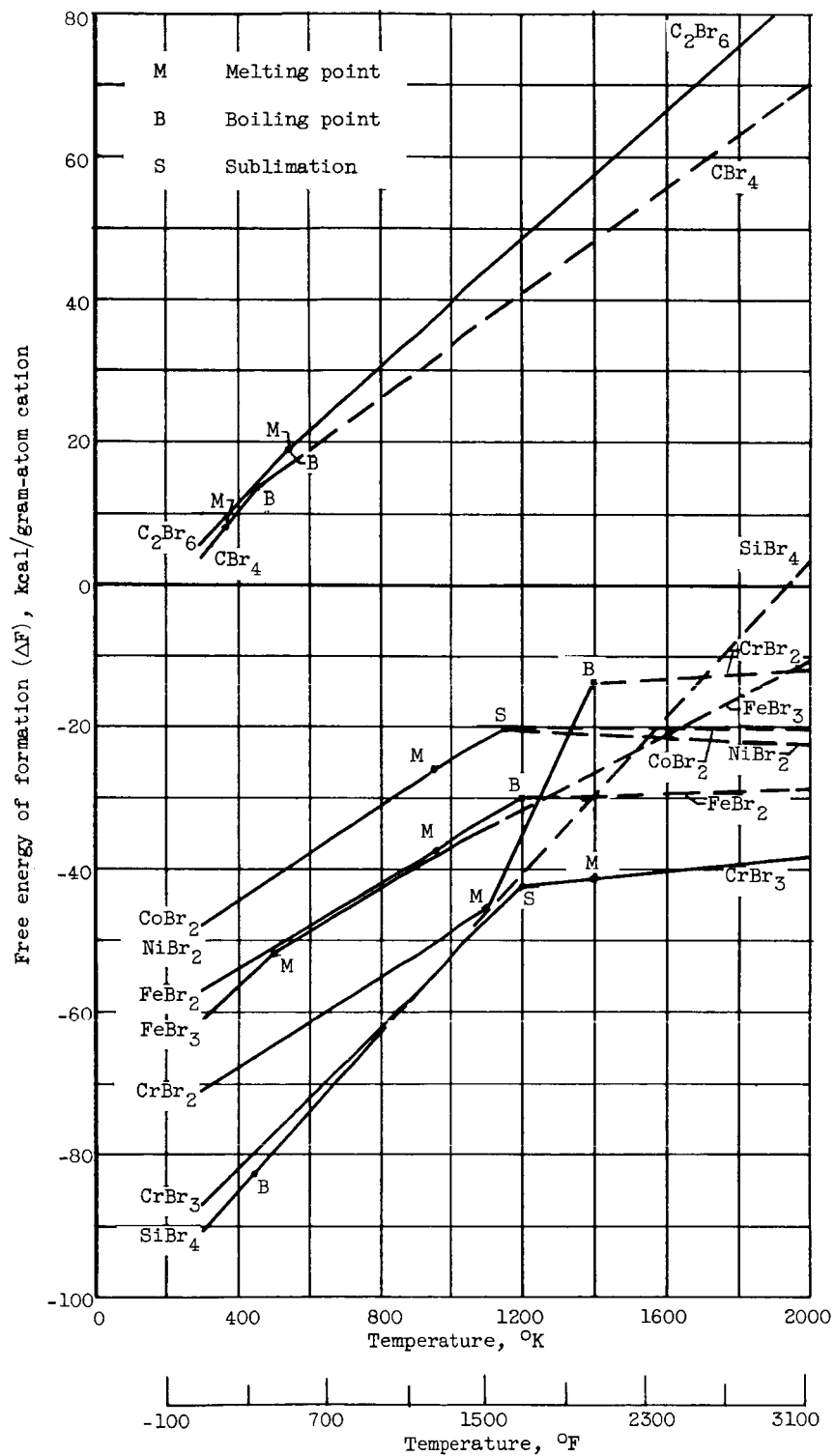
(a) Oxides of cobalt, nickel, iron, chromium, and silicon.

Figure 12. - Standard free energy of formation for various metal oxides up to temperatures of 2000° K.



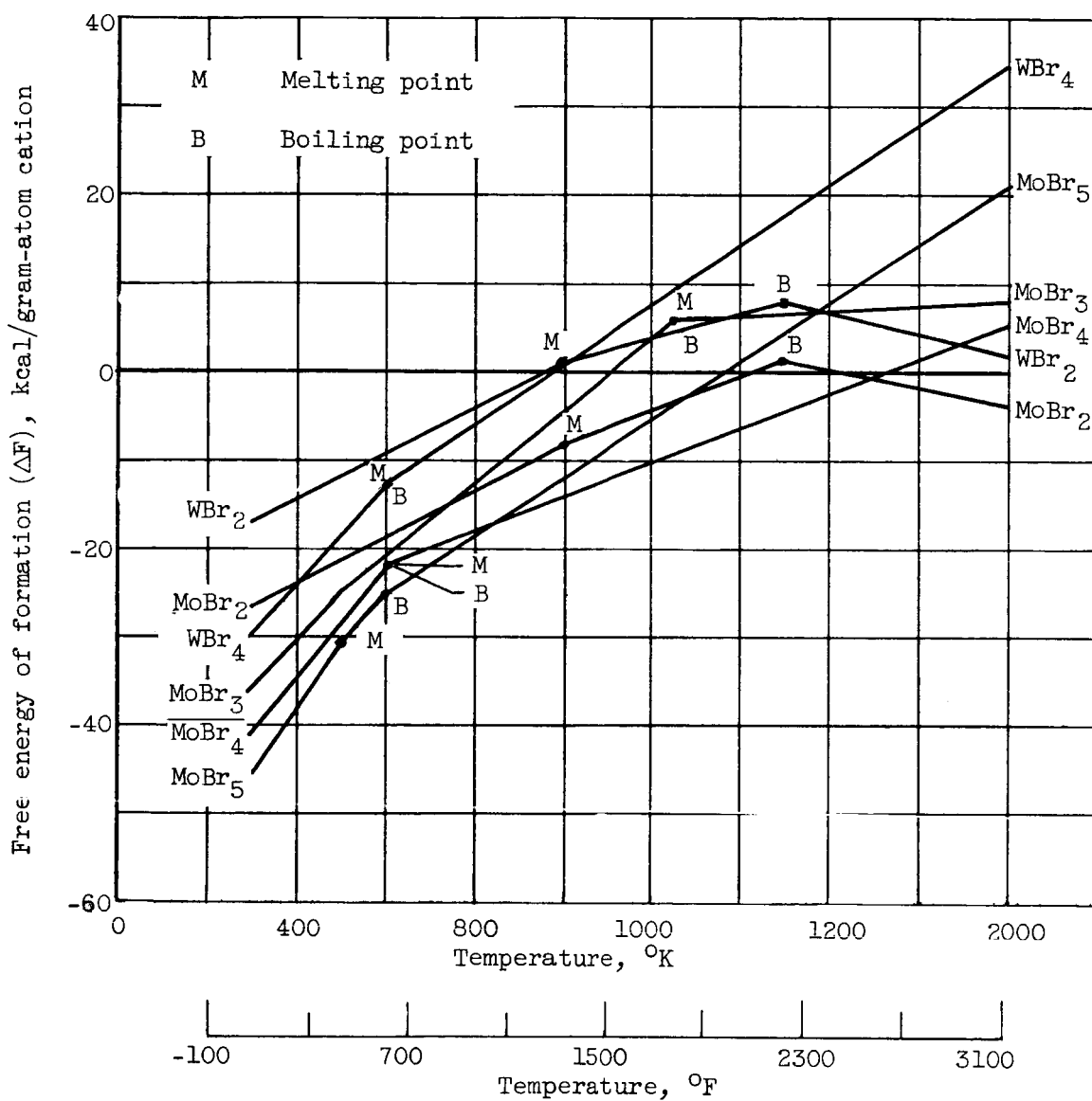
(b) Oxides of molybdenum and tungsten.

Figure 12. - Concluded. Standard free energy of formation for various metal oxides up to temperatures of 2000 $^{\circ}$  K.



(a) Bromides of cobalt, nickel, iron, chromium, and silicon.

Figure 13. - Standard free energy of formation for various metal bromides up to temperatures of  $2000^{\circ}\text{K}$ .



(b) Bromides of molybdenum and tungsten.

Figure 13. - Concluded. Standard free energy of formation for various metal bromides up to temperatures of  $2000^{\circ}\text{K}$ .